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AN ELECTRON PARAMAGNETIC
RESONANCE STUDY OF THE ORDER IN
SEVERAL NEMATIC LIQUID CRYSTALS

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AN ELECTRON PARAMAGNETIC RESONANCE STUDY OF THE ORDER IN SEVERAL NEMATIC LIQUID CRYSTALS

by George C. Fryburg and Edward Gelerinter*

Lewis Research Center

SUMMARY

The molecular ordering in four nematic liquid crystals has been studied as a function of temperature by using an electron paramagnetic resonance technique. The degree of order should be a universal function of the reduced temperature according to Saupe's model. Deviations from this model were observed. The degree of order at any given reduced temperature seemed dependent on the nematic-isotropic transition temperature: the higher the transition temperature, the lower the degree of order. One of the liquid crystals, bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine, exhibited an unusually high degree of order in the lower part of its mesophase. In addition, the EPR lines assumed a peculiar asymmetric appearance. These features can be explained in terms of a model in which the liquid crystal becomes viscous in the lower part of its mesophase.

INTRODUCTION

Several years ago Saupe and Englert (ref. 1) showed that liquid crystals can serve as oriented solvents in magnetic resonance spectroscopy. Because of the orientational order, certain anisotropic terms in the spin Hamiltonian are not averaged to zero. Analysis of the spectra allows evaluation of these anisotropic molecular parameters. In high-resolution nuclear magnetic resonance spectroscopy, the technique has been developed into a method for determining the structure of simple organic molecules (ref. 2). Development in electron paramagnetic resonance (EPR) spectroscopy has not been as spectacular. However, a simple, consistent method of determining the degree of order in a liquid crystal by an EPR technique (refs. 3 and 4) has been devised. The method consists of dissolving in the liquid crystal a small amount (mole fraction $< 10^{-3}$) of a paramagnetic substance that exhibits anisotropic molecular parameters. With a judi-

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cious choice of the paramagnetic probe material, it is possible to relate the order found for the solute to the order of the liquid crystal.

Vanadyl acetylacetonate (VAAC) has been used as a probe because of its essentially planar shape and the fact that it exhibits an anisotropic hyperfine splitting. The vanadium-51 that is responsible for the EPR signal has a nuclear spin of $7/2$ and an electronic spin of $1/2$. The spectrum has been extensively studied (refs. 5 to 7). It consists of eight lines and can be understood in terms of nearly axial "g" and hyperfine tensors. Analysis of the spectrum leads directly to the element of the ordering matrix perpendicular to the molecular plane (ref. 4). Glarum and Marshall (ref. 3) have shown that, with VAAC as a probe, the degree of order determined by this method and its temperature dependence agree closely with that of the pure liquid crystal, as indicated by refractive-index measurements.

The order has been determined as a function of temperature for four different nematic liquid crystals. Their identity and nematic range are presented in table I. The first two were chosen because they are very similar in composition and in nematic range. The third was chosen because it has a very short nematic range, and the fourth, because it has an unusually long range.

The determination of the degree of order as a function of temperature in a liquid crystal is of interest because the magnitude of the degree of order can be related to the angular part of intermolecular potential function (refs. 8 and 9). Thus, experimental values of the order can be used to test the validity of different potential energy functions. However, no correlations have been attempted in this preliminary study.

TABLE I. - LIQUID CRYSTALS AND
THEIR NEMATIC RANGES

Compound	Mesomorphic range, °C
<u>p</u> -(<u>p</u> -ethoxyphenylazo) phenyl hexanoate	75 to 126
<u>p</u> -(<u>p</u> -ethoxyphenylazo) phenyl heptanoate	60 to 119
<u>p</u> -(<u>n</u>)-hexyloxybenzylidene-4-amino-methylbenzene	58.5 to 72.8
bis (4'- <u>n</u> -octyloxybenzal)-2-chloro-1,4-phenylenediamine	59 to 179

EXPERIMENT

The X-band EPR spectra were obtained with a Varian 4502 spectrometer employing field regulation. The samples were heated with a Varian 4547 variable temperature accessory. The sample temperature was measured by means of a 36-gage copper/constantan thermocouple inserted just above the cavity in the nitrogen stream that heated the sample. The sample tubes were designed with 5 millimeters of solid quartz on the bottom to minimize thermal gradients in the sample.

Studies were made of the four liquid crystals listed in table I. Two were very similar; p-(p-ethoxyphenylazo) phenyl hexanoate and the analogous heptanoate. These were used as obtained from Eastman Kodak without further purification. The other two liquid crystals p-(n)-hexyloxybenzylidene-4-amino methybenzene and bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine were of very high purity and were kindly supplied by Dr. S. Arora of the Kent State Liquid Crystal Institute.

The samples were prepared in quartz tubes (4 mm o.d.). A speck of VAAC was first placed in the sample tube, and the liquid crystal was melted into the tube with an air gun modified to regulate the temperature at 100° C. The samples were then degassed by melting under vacuum at 100° C and then back filled with 100 torr of dry nitrogen.

The EPR spectra were usually obtained by heating the liquid crystal into its isotropic phase, lowering the temperature by suitable increments, and then recording the spectra at each temperature after equilibrium had been attained. However, numerous observations indicated that the spectra were identical whether the equilibrium temperature was approached from a higher or a lower temperature. The usual procedure was modified with the bis (4'-n-octyloxybenzal) 2-chloro-1, 4-phenylenediamine as there seemed to be a reaction with the VAAC above 150° C. Reaction was indicated by the appearance of a second spectrum and a darkening of the liquid crystal from its original pale yellow color. With this liquid crystal, the spectra were obtained by heating to the desired temperature and recording after the attainment of equilibrium. The time spent above 150° C was kept at a minimum, and any samples showing discoloration were discarded.

THEORY

VAAC has approximately axial "g" and hyperfine tensors so its spin Hamiltonian may be written as

$$\mathcal{H} = \beta \left[g_{\parallel} H_r S_r + g_{\perp} (H_p S_p + H_q S_q) \right] + A_{\parallel} I_r S_r + A_{\perp} (I_p S_p + I_q S_q) \quad (1)$$

where p, q, r are a set of rectangular axes fixed with respect to the VAAC molecule, and r is the parallel to the $V=O$ bond direction; A_{\parallel} and A_{\perp} , and g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the hyperfine and "g" tensors, respectively, and S and I are the electronic and nuclear spin. If x, y , and z (fig. 1) are a set of axes fixed with the z parallel to the magnetic field H_z , the Hamiltonian may be rewritten as (ref. 10)

$$\begin{aligned} \mathcal{H} = & g\beta H_z S_z + a\vec{I} \cdot \vec{S} + \frac{1}{3}(\Delta g\beta H_z + bI_z)(3\cos^2\theta - 1)S_z \\ & + \left(\frac{b}{2}\right)\sin\theta\cos\theta(I_+e^{-i\varphi} + I_-e^{i\varphi})S_z + \left(\frac{1}{2}\right)(\Delta g\beta H_z + bI_+)\sin\theta\cos\theta(S_+e^{-i\varphi} + S_-e^{i\varphi}) \\ & + \left(\frac{b}{4}\right)\sin^2\theta(I_+S_+e^{-2i\varphi} + I_-S_-e^{2i\varphi}) - \frac{b}{12}(3\cos^2\theta - 1)(I_+S_- + I_-S_+) \end{aligned} \quad (2)$$

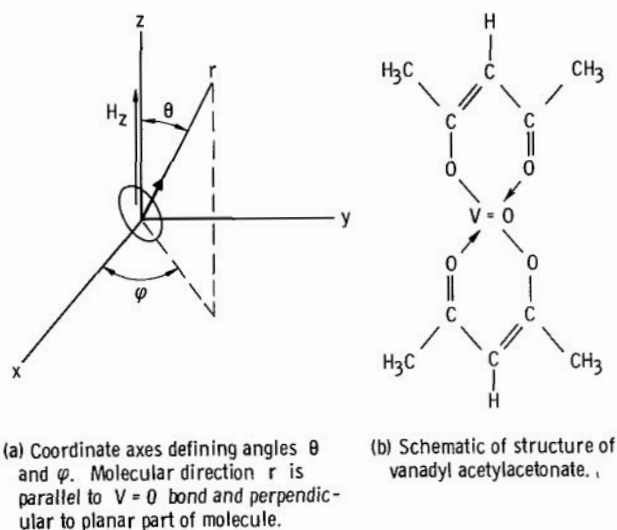


Figure 1. - Geometric illustrations.

where θ is the angle between the z and r axes and φ is the azimuthal angle (see fig. 1) and $g = 1/3(g_{\parallel} + 2g_{\perp})$, $\Delta g = g_{\parallel} - g_{\perp}$, $a = 1/3(A_{\parallel} + 2A_{\perp})$, and $b = A_{\parallel} - A_{\perp}$. The I_{\pm} and S_{\pm} are the nuclear and electronic raising and lowering operators. The assumption $g\beta H \gg b$ allows us to drop all but the first three terms of equation (2). If the VAAC molecule is tumbling freely in an isotropic liquid (e.g., a liquid crystal at a temperature above its clearing point), all the terms of equation (2) average to zero, except for the first two terms which are independent of orientation. If the liquid crystal

is in its mesophase, the molecules are not distributed uniformly in θ , and only the averages over the φ components go to zero. Under these conditions equation (2) may be written as

$$\mathcal{H} = g\beta H_z S_z + a\vec{I} \cdot \vec{S} + \frac{1}{3} (\Delta g\beta H_z + bI_z) \langle 3 \cos^2 \theta - 1 \rangle S_z \quad (3)$$

When Δg is assumed to be zero, equation (3) predicts absorption lines at magnetic fields given by

$$H = \left(\frac{2}{g}\right)H_0 - am_I - \left(\frac{b}{3}\right) \langle 3 \cos^2 \theta - 1 \rangle m_I + \text{terms in } m_I^2 \quad (4)$$

where H_0 is the field corresponding to $g = 2$ at the spectrometer frequency used, and a and b are now in units of gauss. The separation between two lines corresponding to $\pm m_I$ is given by

$$2\langle a \rangle m_I = 2am_I + 2\left(\frac{b}{3}\right) \langle 3 \cos^2 \theta - 1 \rangle m_I \quad (5)$$

or

$$\langle 3 \cos^2 \theta - 1 \rangle = \frac{\langle a \rangle - a}{\frac{b}{3}} \quad (6)$$

where $\langle a \rangle$ is the effective vanadium coupling constant, obtained from the experimental spectra in the nematic phase. Using the previous definitions for a and b , the order parameter can be written as

$$\sigma_z = \frac{\langle 3 \cos^2 \theta - 1 \rangle}{2} = \frac{1}{2} \frac{\langle a \rangle - a}{a - A_\perp} \quad (7)$$

in which $a = -107$ gauss and $A_\perp = -68.5$ gauss (refs. 3, 4, and 7) has been used in these calculations. Complete order corresponds to a value for σ_z of -0.5 . The negative sign indicates that the VAAC tends to align with its plane parallel to the direction of the magnetic field and with the $V = 0$ bond direction perpendicular to the field. Complete dis-

order corresponds to a σ_z of zero. It can be shown that the assumption $\Delta g = 0$ leads to an error in the measured order parameter of less than 1 percent.

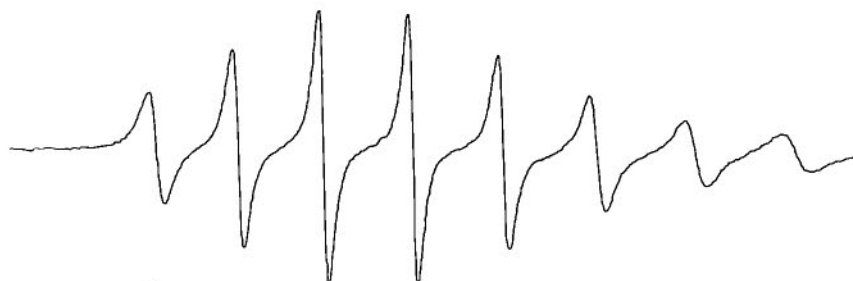
This theory assumes that the solute molecule, VAAC, can tumble freely (i. e., uninhibited by viscous effects, etc). This is essentially the approach taken by Glarum and Marshall (ref. 3) and Chen and Luckhurst (ref. 4). If the opposite assumption is made, namely, that the molecular tumbling is severely hindered, it can be shown that the observed value of the order parameter will approach -0.5. In addition, it can also be shown that the line shapes will become asymmetric.

RESULTS

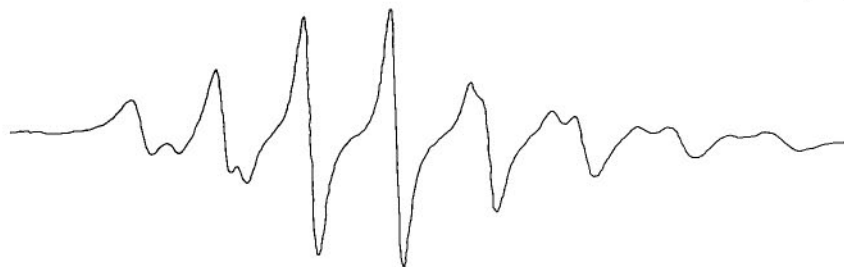
Representative spectra of p-(p-ethoxyphenylazo) phenylheptanoate observed at different temperatures are presented in figure 2. At 135° C (fig. 2(a)), the liquid crystal is in its isotropic phase, and a typical vanadyl spectrum is obtained. At the nematic-isotropic transition point (119° C), both the isotropic and a contracted spectrum are observed (fig. 2(b)). The contraction is indicative that ordering has occurred. The appearance of two spectra is a result of small temperature gradients within the sample. As the temperature is lowered in the nematic region, the spectrum contracts further, indicating an increasing amount of order. This is shown in figure 2(c) taken at 91° C and in figure 2(d) taken at 66° C. The effective vanadium coupling constant $\langle a \rangle$ was obtained from the spectra by measuring the width of the total spectrum in gauss and dividing by 7. The ordering parameter σ_z was calculated from this constant by using equation (7).

The spectra for the p-(p-ethoxyphenylazo) phenyl hexanoate were almost identical with those of the heptanoate, at the same reduced temperatures. The spectra of the p-(n)-hexyloxybenzylidene-4-amino-methylbenzene were also similar. However, the spectra of the bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine were unusual in the lower part of the nematic phase. A series of spectra is shown in figure 3. At 202° C (fig. 3(a)), the liquid crystal is in the isotropic phase, and a typical vanadyl spectrum is obtained. At 155° C, the liquid crystal is in the nematic phase, and the spectrum is a normal contracted spectrum, indicating ordering has occurred ($\sigma_z = -0.22$). But at 91° C (fig. 3(c)), the spectrum has assumed an unusual appearance. The lines have become asymmetric, and the asymmetry is inverted going from one end of the spectrum to the other. At 51° C (fig. 3(d)), this asymmetric line shape is accentuated markedly. The liquid crystal is still in the nematic phase though it has supercooled 8° C below the melting point. The spectrum displays the maximum contraction obtainable and corresponds to nearly complete alinement (i. e., $\sigma_z = -0.50$).

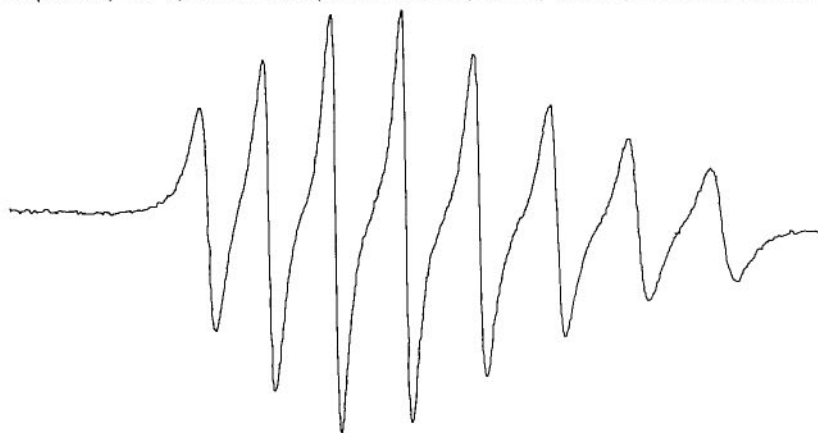
The variation of the ordering parameter with the reduced temperature T^* for the four liquid crystals is shown in figures 4(a) to (d). Here $T^* = T/T_K$, where T_K is



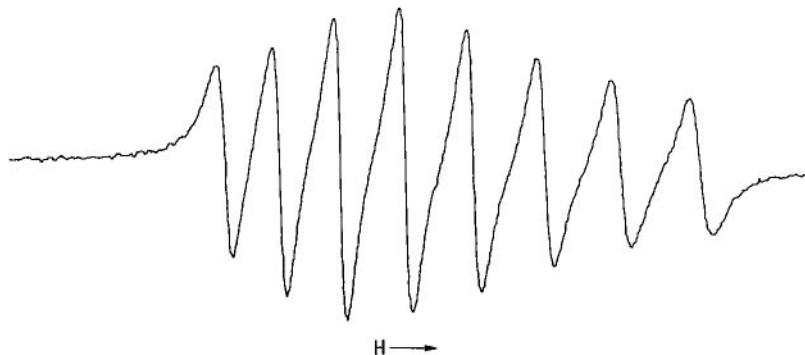
(a) Temperature, 135° C, above nematic-isotropic transition point; spectrum characteristic of isotropic liquid.



(b) Temperature, 119° C, nematic-isotropic transition temperature; double spectrum (isotropic and contracted).



(c) Temperature, 92.5° C, well below clearing point; spectrum characteristic of moderate order, $\sigma_z = -0.32$.

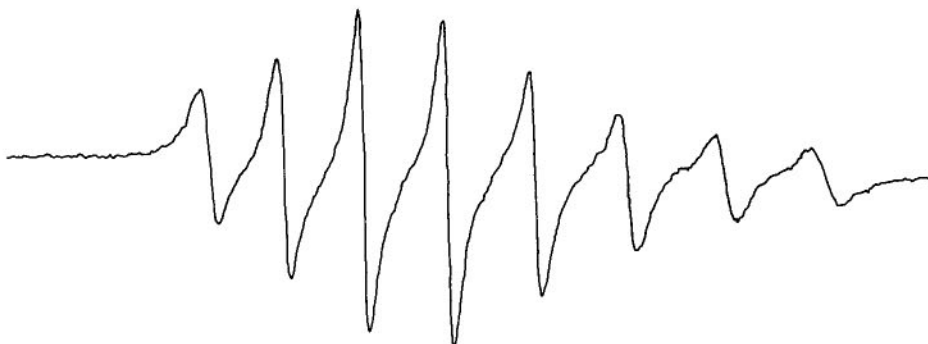


(d) Temperature, 66° C, just above melting point; spectrum characteristic of higher order, $\sigma_z = -0.37$.

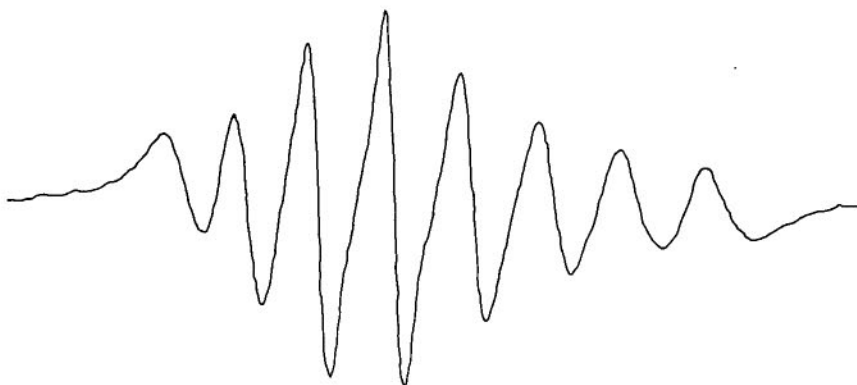
Figure 2. - Experimental derivative spectra of vanadyl acetylacetonate in *p*-(*p*-ethoxyphenylazo) phenyl heptanoate.



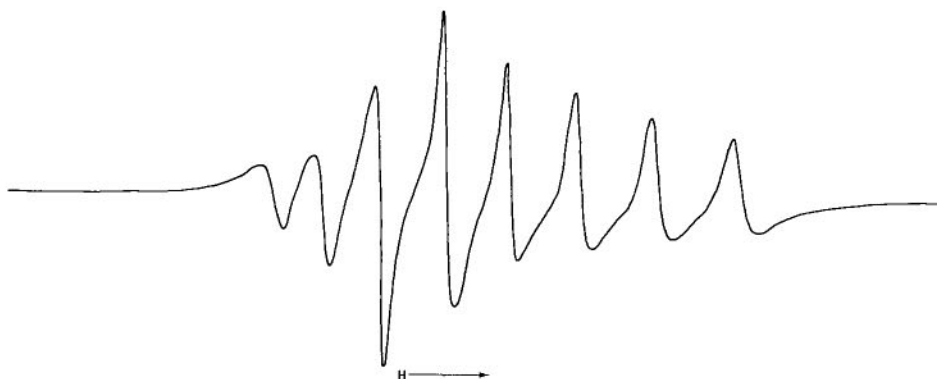
(a) Temperature, 202° C, above clearing point; spectrum characteristic of isotropic liquid.



(b) Temperature, 155° C, just below clearing point; spectrum characteristic of moderate order.



(c) Temperature, 91° C; spectrum characteristic of moderate order but with asymmetric lines.



(d) Temperature, 51° C, just above solidification point; spectrum characteristic of apparent high order, $-a_z \approx 0.50$.

Figure 3. - Experimental derivative spectra of vanadyl acetylacetonate in bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine.

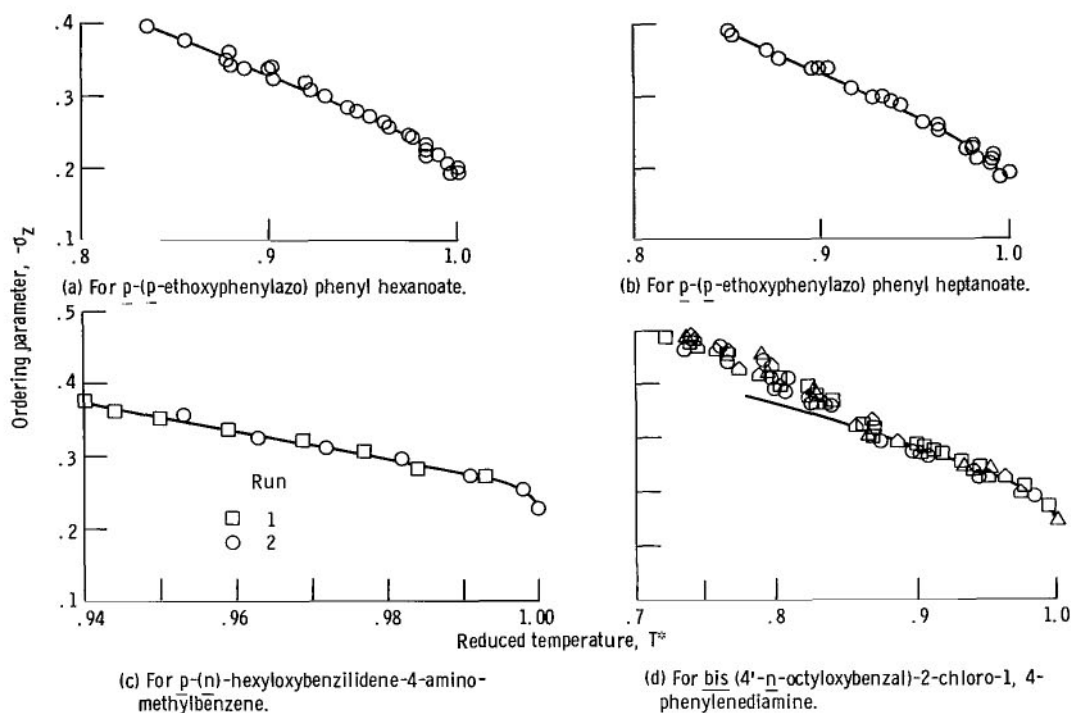


Figure 4. - Ordering parameter $-\sigma_z$ as function of reduced temperature T^* .

the appropriate nematic-isotropic transition temperature in Kelvin. For the p-(p-ethoxyphenylazo) phenyl hexanoate and heptanoate (figs. 4(a) and (b)), the results are nearly identical. The $-\sigma_z$ increases rapidly at the nematic-isotropic transition point ($T^* = 1$) and then increases more slowly in a linear fashion as the temperature is lowered. The results for the p-(n)-hexyloxybenzilidene-4-amino-methylbenzene (fig. 4(c)) are similar. These data include results of two different runs on the same sample, and illustrate the precision obtainable. The variation of $-\sigma_z$ with T^* for the bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine (fig. 4(d)) is similar to the other three liquid crystals in the temperature region $T^* = 1.0$ to about $T^* = 0.85$ ($T = 105^\circ \text{C}$). However, at $T^* = 0.85$ there is a definite break from the linear dependence as the temperature decreases and the values of $-\sigma_z$ are markedly higher than one would expect; in fact, the liquid crystal appears to be approaching complete ordering, $-\sigma_z = 0.5$, near the melting point. These data include results of four different samples. The reproducibility illustrated here is not quite as good as that of the other three liquid crystals, probably due to the reaction effects mentioned previously.

DISCUSSION

The results of the ordering parameter as a function of the reduced temperature for all four liquid crystals are plotted in figure 5 for the purpose of comparison. The curves are smoothed curves taken from the data of figure 4. The curves for the two similar liquid crystals p-(p-ethoxyphenylazo) phenyl hexanoate and heptanoate are identical (solid curve). That for the bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine is somewhat lower (large-dashed curve), and that for the p-(n)-hexyloxybenzylidene-4-amino-methylbenzene is considerably higher (small-dashed curve). According to Saupe's model (ref. 8), the degree of order should be a universal function of the reduced temperature. The results presented here show that there are significant deviations among these liquid crystals. Chen, James, and Luckhurst (ref. 9) have obtained similar results with a set of eight different liquid crystals. They observed that the lower T_K for a given liquid crystal, the higher is the degree of order for a given reduced temperature. Our results corroborate this finding, though the order found for our p-(n)-hexyloxybenzylidene-4-amino-methylbenzene seems to be markedly high. Saupe (ref. 11) also observed deviations from his theory, which he attributed to the rough manner in which the intermolecular interactions were taken into account. It appears that refinements in the intermolecular potentials might be useful.

The most unusual feature of the results is the behavior of the bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine in the lower half of its nematic phase (i. e., the peculiar asymmetry of the spectral lines and the concomitant rise in the ordering parameter $-\sigma_z$). We believe these observations result from the fact that the liquid crystal is so viscous in this region that the probe molecules are hindered from tumbling freely. This situation

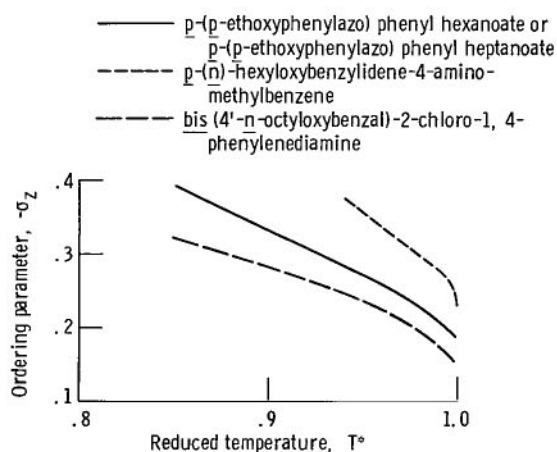


Figure 5. - Smoothed-curve plot of ordering parameter $-\sigma_z$ as function of reduced temperature T^* for all four liquid crystals.

vitiates the calculation of σ_z , and tends to accentuate the perpendicular components of the lines of the spectrum, thus introducing the kind of asymmetry displayed in figure 3(d). It was noted during the degassing of the samples of this liquid crystal that it was much more viscous than any of the other three liquid crystals studied.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 28, 1969,
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